29. *Nitronaphthyl and Aminonaphthyl Alkyl Sulphides.*

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The sodium salts of 1-nitro-2-naphthylthiol and of 4-nitro-1-naphthylthiol react smoothly with methyl and ethyl sulphates to give excellent yields of the thio-ethers. 2-Nitro-1-naphthylthiol, however, is methylated with great difficulty and its ethylation has not been achieved.

EXCELLENT yields of 1-*nitro*-2-*naphthyl* and 4-*nitro*-1-*naphthyl methyl* and *ethyl sulphides* are obtained when the sodium salts of the corresponding thiols react with methyl and ethyl sulphates. The methylation of 2-nitro-1-naphthylthiol failed entirely in ten of the standard methylation methods, but was finally achieved by heating a paste of the slightly moist sodium salt of the thiol with sodium bicarbonate and methyl sulphate. This resistance to methylation may perhaps be due to steric hindrance. All attempts to ethylate this compound failed.

1-*Amino*-2-*naphthyl methyl sulphide* and 4-amino-1-naphthyl methyl sulphide have been satisfactorily diazotised by a modification of the ordinary procedure, which Zincke and Schütz (*Ber.*, 1912, **45**, 477) found to be ineffectual.

The azo-dyes from 4-amino-1-naphthyl methyl sulphide are deeper (bluer) in shade than those from 1-amino-2-naphthyl methyl sulphide. This reversal of anticipated effects appears to indicate a mutual influence of a hypsochromic character between the *o*-azo- and methylthiol groups (cf. Hodgson and Handley, J., 1926, 542; also *J. Soc. Dyers and Colourists*, 1926, **42**, 175, for the same effect in the benzene series).

EXPERIMENTAL.

General Procedure.—The solid mixture (1 g.) of dinitrodinaphthyl mono- and di-sulphides obtained by treatment of a chloronitronaphthalene with alcoholic sodium disulphide is boiled for 5 minutes under reflux with a solution of crystallised sodium sulphide (0·35 g.) and sodium hydroxide (0·2 g.) in alcohol (40 c.c.) and water (6 c.c.), the insoluble monosulphide filtered off, and the filtrate (F) used for the various alkylations described below.

The sequence of three sets of colours which each sulphide gives when treated with cold, hot, and subsequently diluted, sulphuric acid (concentrated), chlorosulphonic acid, and oleum (26%) are placed in this order immediately after the m. p.

4-*Nitro*-1-*naphthyl methyl sulphide.* A solution of sodium hydroxide (5 g.) in water (170 c.c.) was added to F (prepared from 1-chloro-4-nitronaphthalene, 5 g.), and the mixture heated to 60—65° and treated with methyl sulphate (*ca.* 5 c.c.) until the red colour disappeared. Dilution with water (200 c.c.) precipitated nearly pure 4-*nitro*-1-*naphthyl methyl sulphide* (4·0 g.), which crystallised from aqueous alcohol in canary-yellow needles, m. p. 84·5—85° (bright red, yellow, brownish-yellow; bright red, light brown, pink; deep pink, reddish-brown, yellow) (Found : N, 6·6; S, 14·7. $C_{11}H_9O_2NS$ requires N, 6·4; S, 14·6%). The compound is volatile in steam (*ca.* 0·1 g. per l. of distillate), readily soluble in acetone, benzene and chloroform, but less readily soluble in alcohol, ether and glacial acetic acid, and is stable towards sodium in methyl- or ethyl-alcoholic solution.

2-*Nitro*-1-*naphthyl methyl sulphide.* F from 1-chloro-2-nitronaphthalene (1 g.) was treated with hydrochloric acid until it was just acid to litmus; the red colour was discharged and a greenish-yellow solid precipitated. The green filtered solution was diluted with water, and the solid which separated was filtered off as rapidly as possible (if the solution is diluted prior to acidification, a tar is produced), mixed with sodium bicarbonate (3 g.), soaked with methyl sulphate (2 c.c.), and heated for 2 hours on the water-bath; litharge was then added. 2-*Nitro*-1-*naphthyl methyl sulphide* removed by steam-distillation (*ca.* 0·07 g. per l. of distillate), crystallised from aqueous alcohol in small, scintillating, yellow needles (0·1 g.), m. p. 104—105° (deep red becoming pale mauve, light brown, colourless; green, light brown, pale yellow; violet, dirty yellow, colourless) (Found: N, 6·4; S, 14·5. $C_{11}H_9O_2NS$ requires N, 6·4; S, 14·6%), which were readily soluble in acetone, benzene and chloroform, but less readily soluble in alcohol, ether, and glacial acetic acid.

1-*Nitro*-2-*naphthyl methyl sulphide.* F, prepared from 2-chloro-1-nitronaphthalene (5 g.), was treated with sodium hydroxide (5 g.) in water (50 c.c.), and the solution heated to 40—45° prior to the addition of methyl sulphate (*ca.* 5 c.c.) until the reddish-brown colour had disappeared. The precipitated 1-*nitro*-2-*naphthyl methyl sulphide* (3·3 g.) was filtered off, the yield being increased by dilution of the filtrate with water (100 c.c.); it crystallised from aqueous alcohol in long, slender, yellow needles, m. p. 120° (crimson becoming purple, yellow, dark brown; bluish-green, blue, canary-yellow; violet, dark brown, canary-yellow) (Found: N, 6·6; S, 14·6. $C_{11}H_9O_2NS$ requires N, 6·4; S, 14·6%), which were volatile in steam (*ca.* 0·08 g. per l. of distillate), easily soluble in chloroform, fairly soluble in acetone, benzene and ether, but less soluble in alcohol and glacial acetic acid. The sulphide was stable towards sodium in methyl- or ethyl-alcoholic solution.

4-*Nitro*-1-*naphthyl ethyl sulphide* (4·75 g.), prepared in the same way as the methyl homologue, ethyl sulphate (*ca.* 5 c.c.) being used in place of methyl sulphate, crystallised from aqueous alcohol in small yellow needles, m. p. 63° (bright red, orange-yellow becoming colourless, colourless; deep pink, light brown, very pale yellow; deep pink, reddish-brown, pale yellow) (Found: N, 6·1; S, 13·6. $C_{12}H_{11}O_2NS$ requires N, 6·0; S, 13·7%), which were volatile in steam (*ca.* 0·07 g. per l. of distillate), easily soluble in chloroform, fairly soluble in acetone, benzene and ether, but less soluble in alcohol and glacial acetic acid.

1-*Nitro*-2-*naphthyl ethyl sulphide* (3·5 g.), the preparation of which was similar to that of the methyl homologue (ethyl sulphate, *ca.* 5 c.c.), crystallised from aqueous alcohol in long yellow needles, m. p. 87° (maroon becoming yellowish-brown, orange-brown, colourless; dark green, dark brown, bright yellow; brownish-yellow, deep yellow, bright yellow) (Found: S, 13·8. $C_{12}H_{11}O_2NS$ requires S, 13·7%), which were volatile in steam (*ca.* 0·18 g. per l. of distillate), easily soluble in chloroform and benzene, fairly soluble in acetone and ether, but less soluble in alcohol and glacial acetic acid.

Reduction of 4-*Nitro*-1-*naphthyl Methyl Sulphide.*—To 4-nitro-1-naphthyl methyl sulphide (4 g.) dissolved in hot glacial acetic acid (40 c.c.), a solution of crystallised stannous chloride (20 g.) in hydrochloric acid (40 c.c., *d* 1·16) was added gradually to prevent separation of the unchanged substance. The mixture was heated on the water-bath for 15 minutes, the *stannichloride* of 4-*amino*-1-*naphthyl methyl sulphide* separating in colourless needles (3·8 g.), which were filtered off and washed with a little glacial acetic acid [Found: S, 9·0. $(C_{11}H_{12}NS)_2SnCl_6$ requires S, 8·9%]. Reduction in ethyl alcohol was equally efficacious.

The stannichloride was heated to 60° with 5% aqueous sodium hydroxide (60 c.c.), and the mixture cooled and extracted with ether. From the reddish-violet fluorescent extract, dried by anhydrous sodium sulphate, hydrogen chloride precipitated 4-amino-1-naphthyl methyl sulphide hydrochloride (1·6 g.). This crystallised from alcoholic hydrochloric acid in small colourless needles, m. p. *ca.* 220° (decomp.) (pink, bright red becoming yellow, yellow; pink, scarlet becoming yellow, yellow; brownish-red, reddish-orange becoming yellowish-brown, yellow) (Found: Cl, 15·8; S, 14·1. Calc.: Cl, 15·7; S, 14·2%) (cf. Zincke and Schütz, *Ber.*, 1912, **45**, 477). Evaporation of the ethereal solution of the amine left 4-amino-1-naphthyl methyl sulphide; this crystallised from benzene in colourless needles, m. p. 55°, which darkened on keeping (Zincke and Schütz give m. p. 54°) (Found: S, 17·1. Calc.: S, 16·9%), and were very slowly volatile in steam, the milky distillate turning violet in a short time.

4-Amino-1-naphthyl methyl sulphide hydrochloride, when suspended in hydrochloric acid (*d* 1·16) and treated with aqueous sodium nitrite, gave a yellow diazo-solution, which readily coupled with alkaline β-naphthol, Schäffer salt, and " H " acid to give bright red dyes of greater intensity and depth of shade than those from the isomeric 1-amino-2-naphthyl methyl sulphide (Zincke and Schütz, *loc. cit.*, state that the diazotisation is unsatisfactory). The dye with " H " acid was violet by reflected light.

Reduction of 1-*Nitro*-2-*naphthyl Methyl Sulphide.*—The sulphide (4 g.) was reduced as described above except that the heating was continued for 30 minutes; on cooling, 1-*amino*-2-*naphthyl methyl sulphide stannichloride* (5·2 g.) separated in small yellowish-brown crystals, which were washed with a little glacial acetic acid; decomp. *ca.* 195° [Found: S, 9·1. $(C_{11}H_{12}NS)_2SnCl_6$ requires S, 8·9%]. Reduction was less satisfactory in ethyl alcohol.

1-*Amino*-2-*naphthyl methyl sulphide hydrochloride*, obtained in the same way as the isomeride described above, crystallised from alcoholic hydrochloric acid in small colourless needles, m. p. *ca.* 210° (decomp.) (bluish-green, reddish-mauve, pale yellow; pink, scarlet becoming yellow, yellow; deep green, brownish-green, yellowish-brown) (Found: Cl, 15·8; S, 14·1. $C_{11}H_{11}NS,HCl$ requires Cl, 15·7; S, 14·2%), which were soluble in a limited amount of water, excess causing hydrolysis; the solution gave a pink colour and a pink precipitate with ferric chloride. A suspension of the hydrochloride in hydrochloric acid (*d* 1·16) was readily diazotised on addition of aqueous sodium nitrite, and the dyes produced by coupling with alkaline β-naphthol, Schäffer salt, and " H " acid were cherry-red, bright red, and deep bright red by transmitted (violet by reflected) light respectively.

1-*Amino*-2-*naphthyl methyl sulphide* was obtained as a yellow oil, b. p. 235°/753 mm. (Found: S, 17·0. $C_{11}H_{11}NS$ requires S, 16·9%), by distillation of the ethereal solution prepared as for the isomeride above; it darkened on exposure to air and was only very slowly volatile in steam.

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